

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 908 292 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

14.04.1999 Bulletin 1999/15

(21) Application number: 97922161.1

(22) Date of filing: 26.05.1997

(51) Int. Cl.⁶: B29C 49/64, B29C 49/28(86) International application number:
PCT/JP97/01751(87) International publication number:
WO 97/45246 (04.12.1997 Gazette 1997/52)(84) Designated Contracting States:
DE FR GB(30) Priority: 28.05.1996 JP 133491/96
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40593 Düsseldorf (DE)**(54) METHOD AND APPARATUS FOR PRODUCING A BLOW MOLDED ARTICLE**

(57) Provided is a method for producing blow moldings having a relatively large size through blow molding by use of a simple facility. Faithful mold-to-resin transfer of a surface such as a glossy surface is attained, and moldings can be obtained in shorter cycles with improved productivity. The method comprising the steps of feeding a melt parison of crystalline resin into the space between molds, clamping the molds, blowing a pressurized fluid into the interior of the parison so as to cause the parison to be into close contact with the inner surfaces of the molds and to solidify the parison, wherein, while the parison and the mold inner surfaces are in close contact, the temperature of inner surfaces of the molds is maintained at a temperature from a temperature 10°C lower than the crystallization temperature of the crystalline resin to the melting point of the resin, and the parison is removed from the molds after the parison is cooled through introduction thereof or discharge therefrom, during or after blowing-in of the pressurized fluid, of a cooling medium not higher than room temperature. An apparatus comprises a blow molding machine; a forming mold which is used in combination with the blow molding machine for producing a blow molding, the forming mold having degassing pores having a diameter of 100 μm or less in the surface of the mold at intervals (a pitch) of 50 mm or less; and means for introducing and discharging a cooling medium into or from a parison formed through the mold.

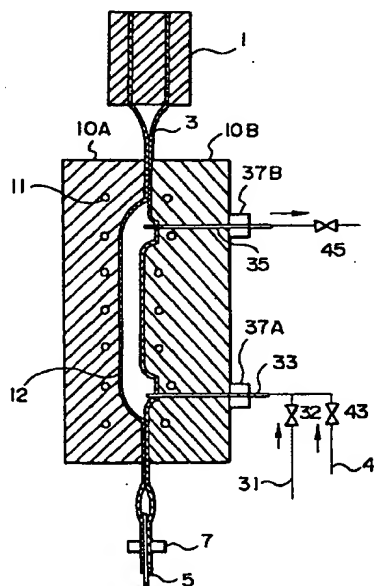


FIG. 2

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Description

Field of the invention:

[0001] The present invention relates to a method and an apparatus for producing blow moldings by use of crystalline resin. Particularly, the method and apparatus for producing blow moldings according to the present invention provides excellent accuracy in transfer of the shape of a mold inner surface (hereinafter called "mold transferability") for a glossy surface, an embossed surface, and like surfaces, through employment of specific molding conditions, and remarkably shorten the molding cycle time.

Background art:

[0002] Blow molding has conventionally been used in manufacture of different types of containers and similar articles due to its variety of advantages; it enables production of blow moldings under low pressure to thereby reduce the mold costs, and it improves the strength and rigidity per unit weight due to reduction in weight of moldings. Further, in recent years, blow molding of automobile parts such as bumpers, spoilers, and wheel caps has become of interest. Demands in this field include reduction of molding cycle time for large moldings such as bumpers, and development of a method of manufacturing moldings having excellent appearance such as high surface gloss and the like for spoilers and wheel caps.

[0003] In the case in which crystalline resins such as polypropylene resins and polyamide resins are used in manufacture of automobile parts, which require strength and rigidity, even if a mold having a mirror-polished mold inner surface is used, ordinary molding conditions cannot avoid occurrence of melt fractures, die lines, or pockmark-like patterns in resultant blow moldings due to inclusion of gas or crystallization. Thus, in blow molding of a crystalline resin, faithful transfer of mold inner surface can hardly be attained, making difficult the manufacture of blow moldings having excellent appearance in terms of surface gloss and the like.

[0004] Japanese Patent Publication (*kokoku*) No. 2-40498 describes a method for producing blow moldings having excellent surface gloss. According to the method, a parison having a great number of fine projections and depressions (depth: 2-100 μm) in its resin surface is set in molds which are mirror-polished to have a mirror surface of 0.5 S or less and heated to a temperature higher than the crystallization temperature of the resin; blow molding is carried out; and the molds are cooled to a temperature lower than the crystallization temperature. However, this method has disadvantages; surface conditions of a parison must be regulated, resins are limited to those suffering melt fracture upon molding, and molding cycle is long, thereby reducing productivity in manufacture of large moldings such as automobile parts.

[0005] In order to improve the surface properties of a blow molding formed of crystalline resin, a conceivable method is one in which a melt parison is used in blow molding and the mold temperature is maintained higher than the crystallization temperature of the crystalline resin when the parison and the molds are in close contact. This method inevitably prolongs the molding cycle. To solve this problem, there have been proposed various methods for effectively cooling the molds heated at a temperature higher than the crystallization temperature to thereby maintain the shape of the molded article. For example, the invention disclosed in Japanese Patent Publication (*kokoku*) No. 7-77728 is directed to a method in which a high-temperature oil and a low-temperature oil are used as heat media for regulating temperature of molds, and upon switching of the oils, the flow path of the heat media are air-blown. Another invention, which is disclosed in Japanese Patent Application Laid-Open (*kokai*) No. 6-226828, is directed to a molding method in which molds are heated by use of steam and cooled by use of water. However, these methods in which heating and cooling of molds are performed repeatedly require a plurality of media for heating and cooling, or regulation of temperature of molds over a wide range. Therefore, these methods still have room for improvement in view of the intricate equipment and operation involved. Moreover, repetition of heating and cooling may prevent successful reduction in cycle time of molding. Japanese Patent Application Laid-Open (*kokai*) No. 4-77231 discloses a blow molding method in which a parison formed of a soft resin containing a crystalline resin is fed into the space between molds, followed by clamping of the molds, and a fluid is pressure-blown into the interior of the parison so as to cause the parison to come into close contact with the mold inner surfaces to thereby carry out molding and cooling, wherein the temperature of the molds is maintained between a temperature in the vicinity of the temperature at which the crystallization rate of the crystalline resin is the highest and the melting point of the crystalline resin, and a fluid serving as a cooling medium is pressure-blown into and circulated within the interior of the parison under pressure. This method may be effective for reducing die lines or weld lines in the surface of a molding; however, for pressure-blowing a cooling medium this method uses two blowing needles of different pressures, and therefore, circulation of the cooling medium occurs only at the initial stage of cooling. Also, since the cooling medium is rapidly heated upon contact with the high-temperature parison, the cooling efficiency is not always satisfactory and thus the reduction in time of molding cycle is limited. Therefore, there remain problems for satisfactory application to production of large blow moldings.

[0006] Japanese Patent Application Laid-Open (*kokai*) No. 6-226829 discloses a method in which a liquid-nitrogen-

vaporized gas is fed inside a parison through one of two high-pressure blow pins extending to the interior of the parison and the gas is discharged through the other blow pin, to thereby cool the parison while reducing the molding cycle. However, that patent application discloses no technical concept for attaining both the reduction of molding cycle time and the improvement of mold transferability by regulating the mold inner surface temperature in response to the crystallization temperature of the crystalline resin.

SUMMARY OF THE INVENTION

[0007] Under these technical circumstances, an object of the present invention is to provide a method and an apparatus for producing blow moldings weighing 500 g or more, especially large blow moldings weighing 1 kg or more, with a shortened molding cycle, at higher productivity, and with improved surface transfer of a glossy surface, an embossed surface, or the like.

[0008] The present inventors conducted careful studies on a method and an apparatus for producing blow moldings through use of crystalline resin, especially large blow moldings, which enables a shortening in molding cycle time and achievement of improved surface transfer of a glossy surface, an embossed surface, and the like. As a result, they found that the molding cycle time and the appearance of moldings are satisfactorily improved if temperature conditions of the mold inner surfaces—inner surfaces—of the molds (hereinafter referred to as "inner surfaces of molds" or "mold inner surfaces" for the sake of clarity) are properly determined so as to match the properties of the crystalline resin; if cooling of the interior of the parison is performed in a more efficient manner; and if fine pores having a specific diameter are formed at specific intervals in the mold inner surface, thus leading to completion of the present invention. Accordingly, the present invention provides a method and an apparatus for producing blow moldings through a blow molding method, which realizes excellent mold transferability and shortened cycle time of molding.

[0009] According to a first aspect of the present invention, there is provided a method of producing a blow molding, the method comprising the steps of feeding a melt parison of crystalline resin into the space between molds, clamping the molds, blowing a pressurized fluid into the interior of the parison so as to cause the parison to come into close contact with the inner surfaces of the molds and to solidify the parison, wherein, while the parison and the mold inner surfaces are in close contact, the temperature of inner surfaces of the molds is maintained at a temperature within the range from a temperature 10°C lower than the crystallization temperature of the crystalline resin to the melting point of the crystalline resin, and the parison is removed from the molds after the parison is cooled through introduction thereinto or discharge therefrom, during or after blowing-in of the pressurized fluid, of a cooling medium whose temperature is not higher than room temperature.

[0010] Preferably, the molds have degassing pores having a diameter of 100 μm or less in the surfaces of the molds at intervals (a pitch) of 50 mm or less.

[0011] According to a second aspect of the present invention, there is provided an apparatus for the production of a blow molding, which apparatus includes a blow molding machine; a forming mold which is used in combination with the blow molding machine for producing a blow molding, the forming mold having degassing pores having a diameter of 100 μm or less in the surface of the mold at intervals (a pitch) of 50 mm or less; and means for introducing and discharging a cooling medium into or from a parison formed through the mold.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIGS. 1 and 2 are sectional views showing an embodiment of the method and apparatus for producing blow moldings according to the present invention, wherein

FIG. 1 shows steps of mold opening and parison feeding; and

FIG. 2 shows steps of clamping, molding, and cooling.

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] Embodiments of the present invention will next be described.

[0014] Crystalline resins which are used in the production method of the present invention are not particularly limited; there may be used polyolefin resins, polyamide resins, polyester resins, and polyacetal resins. Examples of polyolefin resins include homopolymers of α -olefins such as ethylene, propylene, butene-1, 3-methylbutene-1, 3-methylpentene-1, and 4-methylpentene-1; copolymers of these α -olefins; and copolymers of these α -olefins and other unsaturated monopolymers that are copolymerizable therewith. Typical examples of polyolefin resins include high-, medium-, and low-density polyethylene resins, linear low-density polyethylenes, super molecular weight polyethylenes, ethylene-vinyl acetate copolymers, and ethylene-ethyl acrylate copolymers; polypropylene resins such as syndiotactic polypropyl-

enes, isotactic polypropylenes, and propylene-ethylene random or block copolymers; and poly4-methylpentene-1.

[0015] Examples of polyamide resins include ring opening polymerization products of cyclic aliphatic lactams, such as 6-nylon and 12-nylon; polycondensation products of aliphatic diamine and aliphatic dicarboxylic acid, such as 6,6-nylon, 6,10-nylon, and 6,12-nylon; polycondensation products of aromatic diamine and aliphatic dicarboxylic acid, such as those between m-xylenediamine and adipic acid; polycondensation products of aromatic diamine and aromatic dicarboxylic acid, such as those between p-phenylenediamine and terephthalic acid and those between m-phenylene-diamine and isophthalic acid; and polycondensation products of amino acids, such as 11-nylon.

[0016] Examples of polyester resins include polycondensation products of aromatic dicarboxylic acid and alkylene glycol, and specific examples include polyethylene terephthalate and polybutylene terephthalate.

[0017] Examples of polyacetal resins include homopolymers such as polyoxymethylene; and formaldehyde-ethylene oxide copolymers which are obtained from trioxan and ethylene oxide.

[0018] In the production method of the present invention, the above-mentioned crystalline resins may be used singly or in combination. Further, if necessary, other resins having low crystallinity, amorphous resins, elastomers mentioned below, inorganic fillers, and a variety of additives may be added to the crystalline resins. Of the listed thermoplastic resins, preferred are polypropylene resins such as polypropylene, block or random copolymers of propylene and other olefins, and mixtures of these copolymers. Polypropylene resins containing acid-modified polyolefin resins which have been modified with unsaturated carboxylic acids or their derivatives may also be used.

[0019] Preferably, polypropylene resins have a melt index MI (230°C, 2.16 kgf) of 0.1-2.0 g/10 min, more preferably 0.2-1.0 g/10 min, from the viewpoint of blow moldability including drawdown resistance. Further, moldability and the like can be improved through addition of a high density polyethylene resin having a melt index MI (190°C, 2.16 kgf) of 0.001-1 g/10 min, preferably 0.01-0.5 g/10 min, to a raw molding material in an amount of 0-30% by weight. Elastomers having a Mooney viscosity (ML₁₊₄ 100°C) of 10-120 may also be added to the raw molding material, wherein the elastomers include ethylene-propylene copolymer elastomer, ethylene-propylene-diene copolymer elastomer, styrene-diene elastomer, or hydrogenated elastomers of these elastomers.

[0020] Moreover, inorganic fillers may be added to the raw molding material in an amount of 0-50% by weight in order to improve rigidity, strength, heat resistance, etc. of blow moldings. Specific examples of the inorganic fillers include talc, mica, calcium carbonate, glass fiber, carbon fiber, magnesium sulfate fiber, potassium titanate fiber, titanium dioxide fiber, magnesium oxysulfate fiber, and organic fiber. Of these materials, talc, mica, and glass fiber are preferably used. Further, if necessary, there may be added stabilizers, antistatic agents, weather-proof agents, flame retardants, pigments, dispersing agents, or crystal nucleation agents. Examples of the crystal nucleation agents include talc, alkali metal salts of organic carboxylic acid, basic polyvalent metal salts of cyclic phosphoric esters, aluminum 4-tert butyl benzoates, dibenzylidene sorbitols, and their derivatives.

[0021] In the production method of the present invention, the terms "crystallization temperature" and "melting point" refer not only to those of crystalline resins *per se* used in the present invention, but also to those of raw material resins which are actually subjected to blow molding and which contain, in addition to a crystalline resin, crystal nucleation agents for improving crystallinity, other thermoplastic resins, fillers such as talc, etc. In the case of a raw material for blow molding composed of two or more crystalline resins, measurements of crystallization temperature and melting point by differential scanning calorimetry (DSC) may show two or more peaks. In such a case, the highest crystallization temperature, the highest melting point, or the crystallization temperature and the melting point of the predominant resin component are employed as the crystallization temperature and melting point as defined in the present invention.

[0022] In the present invention, a blow molding machine is used to produce blow moldings from a crystalline resin which is selected in accordance with the use, shape, and size of the target blow molding.

[0023] An example production method will next be described with reference to FIGS. 1 and 2. First, a crystalline resin is melt-extruded from an extruder. Typically, by use of an accumulator the crystalline resin is extruded through a die (1) into the space between opened molds (10A and 10B) which are used in combination, and is formed into a tubular parison (3). Subsequently, the lower end portion of the parison (3) is pre-pinched with a pinch (7) to prevent a blown-in fluid from escaping. Simultaneously, a fluid feeding pipe (5) for pre-blowing the parison is pinched. The parison is then expanded to a certain extent by pre-blowing, and, as shown in Fig. 2, is clamped by the set of molds whose mold inner surfaces (12) are regulated to have a certain temperature by a heating means (11). Subsequently, a conduit (33) of a pressurized fluid and a cooling medium is caused to penetrate through the wall of the parison by a thrusting apparatus (37A), and the pressurized fluid is blown via a pressurized fluid feeding path (31) and a valve (32) into the cavity of the parison so as to cause the parison to come into close contact with the mold inner surfaces (12). The fluid for blowing-in is not particularly limited. Generally, air at room temperature is used in consideration of mold transferability. In order to reduce the molding cycle time, there may be used a fluid of the same type as that used as a cooling medium for forced cooling of the interior of a blow molding as described below.

[0024] Subsequently, a discharge pipe (35) is inserted into the interior of the parison by use of a thrusting apparatus (37B). Next, the valve (32) of the pressurized fluid feeding path is shut, and a valve (43) of a cooling medium feeding path (41) is opened for introduction of the cooling medium into the interior of the parison. The interior of the parison is

forcedly cooled through circulation and discharge of the cooling medium while the pressure of the cooling medium is regulated by a discharge valve (45) and the internal pressure is maintained. When cooling enables mold release of a blow molding, the molds are opened and the blow molding is removed. Timely mold-opening is achieved through measurement of the temperature of the discharged cooling medium or a like procedure. In this connection, cooling of molds is substantially unnecessary, but may be performed, as an auxiliary procedure, according to the size, shape, wall thickness, and like factors of molding.

[0025] Next will be described the production method of the present invention, including the temperature of mold inner surfaces and the method for cooling the interior of the parison.

[0026] First, when the parison is brought into close contact with the mold inner surfaces, the temperature of the mold inner surfaces is required to fall within the range from a temperature 10°C lower than the crystallization temperature of the crystalline resin to the melting point of the crystalline resin. This temperature is not particularly limited so long as it falls within the above-mentioned range; however, when reduction in time of molding cycle is of particular interest, the temperature is regulated to fall within the range of crystallization temperature $\pm 10^\circ\text{C}$, preferably the range from "crystallization temperature - 5°C" to "crystallization temperature + 10°C." An optimum temperature is selected within the above-mentioned ranges, in consideration of the degree of accuracy in mold transfer, conditions of mold inner surfaces (mirror surfaces, embossed surfaces, surfaces with patterns or characters), type of crystalline resin, resin temperature during molding, or size or wall thickness of the molding.

[0027] The heating method of the mold inner surfaces is not particularly limited, and there may be employed any method for heating the entirety of molds; for example, a method in which an ordinary heating medium such as water is circulated, or a method in which electrical heating such as resistance heating and dielectric heating is employed. Further, there may be used a method for heating selected portions of the mold inner surfaces, such as gas-flame heating. Alternatively, a combination of the above-mentioned methods may be used.

[0028] In the production method of the present invention, cooling of molds after the close contact between the molds and the parison is substantially unnecessary. Therefore, a specific mold structure, equipment, or control for temperature regulation in heating and cooling of molds can be eliminated, resulting in a simplified molding facility. However, if necessary, or as a supplementary procedure, after the parison is brought into close contact with mold inner surfaces, the molds may be cooled such that the mold inner surfaces come to have a temperature lower than that as measured when the parison comes into close contact with mold inner surfaces; for example, a temperature lower than the crystallization temperature of the crystalline resin, or a temperature 10°C or more lower than the crystallization temperature of crystalline resin. In this case, there is preferably employed a method in which a cooling medium is circulated after purge of a heating medium.

[0029] Concerning heating of molds, so long as the mold inner surfaces are maintained at a specific temperature during transfer from the molds to the resin molding (i.e. when the resin molding is brought into close contact with the molds; hereinafter may be simply referred to as "upon close contact"), there may be preferably employed a mold structure having a small heat capacity, i.e., a mold structure in which the surface temperature changes considerably after the close contact takes place. In this case, the mold inner surface temperature may temporarily rise due to the heat from the melt resin. In such a case, even if the mold inner surface temperature is lower than the crystallization temperature of the crystalline resin, satisfactory transferability is secured. Therefore, the mold inner surface temperature is preferably set as low as possible, from the viewpoint of molding cycle time. However, the mold inner surface temperature upon close contact is required to fall within the range from a temperature 10°C lower than the crystallization temperature of the crystalline resin to the crystallization temperature of the crystalline resin.

[0030] Such a mold structure is also effective for reducing time required for the mold inner surfaces to become ready for releasing the molded product by forced cooling of the interior of the parison after completion of the mold-to-resin transfer.

[0031] In other words, in the production method of the present invention, the mold inner surface temperature is maintained within a specific temperature range only upon close contact, and preferably, heat transfer from the molds to the molding should be avoided during subsequent cooling. For this purpose, there is advantageously employed a mold structure having a relatively thin metallic portion of the mold inner surfaces and comprising an air chamber for heat insulation or a heat insulating material.

[0032] As required, before die closing, the tip end of a parison is press-fused for sealing the parison, and a gas is pre-blown into the sealed parison so as to expand the parison or enlarge the diameter of the parison.

[0033] In the production method of the present invention, forced cooling of a blow molding is performed as follows: during or after blowing-in of a pressurized fluid, a cooling medium under pressure is introduced into the interior of the parison, and thereafter or simultaneously therewith, the heated medium in the parison is discharged through a discharge port provided at a place distant from an introduction port of the cooling medium. With this cooling method, the cooling medium is circulated within the interior of the parison, whereby effective cooling can be performed. The cooling medium is not particularly limited, and there may be used air, carbon dioxide gas, or nitrogen gas having a temperature of room temperature or lower. Preferably, air cooled to -20°C or less, more preferably -30°C or less, is used.

[0034] Generally, the pressure of the introduced cooling medium falls within the range so as to make the internal pressure of the parison 2-10 kg/cm², and may be selected as adequate according to the size and wall thickness of the product blow molding and the type of crystalline resin. In consideration of transferability of mold inner surfaces, reduction of molding cycle time, and like factors, the internal pressure of the parison at the early stage of coolant introduction is at a relatively high level; at least 4 kg/cm², preferably 4-10 kg/cm², more preferably 5-8 kg/cm².

[0035] Preferably, after transfer of the mold inner surfaces, as required for retention of the shape of a blow molding, the internal pressure of the parison is reduced below the pressure as measured at the beginning of introduction of a cooling medium; for example, lower than 4 kg/cm². Specifically, the internal pressure of the parison is maintained at 4-10 kg/cm², preferably 5-8 kg/cm², for a period of 10-30 seconds following introduction of the cooling medium, and thereafter is preferably lowered below the pressure as measured at the time of introduction of the cooling medium. Generally, the control of the internal pressure of the parison is performed through regulation of the amount of discharge while the amount of introduction is maintained constant; this control is important for reduction of molding cycle time achieved by a process in which the amount of discharge is increased after completion of mold-to-resin transfer so as to lower the internal pressure of the parison, to thereby increase the circulation amount and improve the cooling efficiency. Further, after completion of cooling of the parison, the control contributes to the reduction of time required for release of the internal pressure and further to reduction of the molding cycle time. The introduction and discharge of cooling medium are characterized in that the cooling medium introduced into the parison is caused to travel directionally (for example, in a single direction). Also, unlike the conventional circulating method limited to the interior of the parison, the parison is always cooled by fresh, low-temperature cooling medium. According to the size and shape of the molding, the conditions may be changed; for example, the introduction port and discharge port are alternated during cooling. Cooling from inside the parison enables very efficient cooling as compared with cooling of molds, as a result of a direct contact between the cooling medium with the inner surface of a parison, creation of a flow of the cooling medium (circulation and turbulence), and an increase in flow rate. For example, introduction of a cooling medium at -30°C provides a discharge gas of about 90°C.

[0036] In the present invention, forced cooling of the interior of the parison is generally performed as follows: a cooling medium introduction needle (pipe) provided in the wall of a mold is caused to move toward the parison and penetrate through the wall of the parison. The discharge needle (pipe) is similarly provided. The introduction needle (pipe) and the discharge needle (pipe) may be provided separately, or they may be formed into a double pipe. Generally, in order to enable the medium to flow within the blow molding so as to uniformly cool the entirety of the inner wall of the molding, the arrangement, location, number, and size of the introduction/discharge pipes are determined as adequate in consideration of the shape, etc. of the molding. In the present invention, the pipes are advantageously provided separately in consideration of cooling efficiency. Further, if necessary, there may be employed means which advances, retreats, or rotates (i.e., rotates a needle having an opening in the side surface) the cooling medium introduction needle inside the parison, or means which introduces the cooling medium intermittently.

[0037] In addition to the forced cooling of the interior of the parison, in the present invention degassing pores are advantageously provided in the mold inner surfaces, in order to reduce molding cycle time, attain more advanced improvement of the degree of close contact (transferability), or to provide even better appearance of moldings. The pores improve transcription of the portions where gases tend to remain, such as depressed portions having sharp curves. As a result, the surface conditions of a blow molding become excellent even if the molding has a complex structure.

[0038] Conventionally, pores having a diameter of about 0.2-0.5 mm have typically been employed as the degassing pores. However, the degassing pores in the present invention preferably have a diameter of 100 μm or less, more preferably 80 μm or less. If the diameter is in excess of 100 μm, a "hair" of resin (hair-shaped projections) may be generated on the surface of a molding. The possible lower limit of the diameter of degassing pores is about 10 μm, which is the limit of precise machining. The depth of degassing pores is generally 0.2-0.5 mm, and the pores may be formed through laser beam machining, electroforming, or like processing.

[0039] The pitch (interval) between degassing pores is preferably 50 mm or less, more preferably 30 mm, most preferably 20 mm. If the pitch is in excess of 50 mm, haze is generated on the surface of a molding due to insufficient degassing. The lower limit of the pitch is not particularly limited, and the pitch may be about 3 mm. However, since a smaller pitch increases the mold price, the pitch is determined as adequate in consideration of its potential effects on modification of the surface of the molding. The degassing pores are not required to be distributed uniformly on the entirety of mold inner surfaces, and are preferably formed at the portions such as depressions having sharp curves where intensive degassing is required.

[0040] Further, the mold inner surfaces may be machined to have a variety of surface conditions corresponding to the target molding product. Examples of the machining include mirror polishing to 0.5 S or less, embossing, pattern (or impression) machining, character/figure machining, and a combination thereof.

[0041] Next will be described cooling of the inner wall of a parison and mold release. Conventionally, in order to reduce the cycle time of molding, there has been employed a method of cooling a parison through regulation of the mold tem-

perature to a temperature lower than the crystallization temperature of the crystalline resin, specifically at least about 30°C lower than the crystallization temperature. With such a conventional cooling method, the parison is cooled mainly by the molds. In contrast, in the present invention, without cooling from the molds, crystallization of the inner wall of the parison efficiently proceeds through forced cooling from inside the parison. Therefore, since the molding can be shaped even when the apparent mold inner surface temperature is around the crystallization temperature, the molding can be released from the molds and removed.

[0042] Consequently, repetition of heating and cooling of molds as performed in conventional methods is eliminated, resulting in a reduction of the cycle time of molding. In addition, low-cost production is achieved in combination of simplification of manufacturing machinery and a temperature control method.

[0043] After the parison has been completely cooled, the supply of the cooling medium into the interior of the parison is stopped; the medium is discharged; the molds are opened; and the molding is removed.

[0044] As described above in detail, according to the method of producing blow moldings of the present invention, blow moldings having excellent surface gloss and appearance are produced at high productivity, due to the combination of means for enhancing transcription by use of a specific mold inner surface temperature and means to efficiently cool the blow moldings through forced cooling of the interior of a parison, and also due to the provision of specific degassing pores in the surfaces of the molds. Moreover, moldings having a relatively thick wall or large moldings can be produced in a reduced molding cycle at high productivity.

[0045] The production method of the present invention can be used to produce any type of known moldings which can be produced through blow molding. In the moldings, the resin layer may be either single-layered or multi-layered; however, in the case of multi-layered resin, the outermost layer must be made of a crystalline resin. The structure of the cavity of the molding may be determined arbitrarily, and the molding may have a plurality of cavity portions.

[0046] Next will be described a production apparatus of the present invention. The production apparatus of the present invention comprises a blow molding machine, molds having a specific structure, and means for introduction of a cooling medium into and discharge thereof from the interior of a parison.

[0047] The blow molding machine is not particularly limited, and a molding machine used in the "Examples" section of the present invention may be advantageously used.

[0048] The molds which are used in the production apparatus of the present invention produce blow moldings when used in combination with the blow molding machine. The molds have in the surfaces degassing pores having a diameter of 100 μ m or less at a pitch of 50 mm or less. The diameter, pitch, and other factors of the degassing pores are as described above.

[0049] Means for introducing a cooling medium into a parison and discharging the medium therefrom may be provided in the die of the blow molding machine, through the mold wall, or both; however, the introduction means and discharge means must be provided separately. Generally, these means are an introduction needle (pipe) and a discharge needle (pipe). These needles (pipes) may be provided separately, or may be in the form of a double pipe. Generally, in order to enable the medium to flow within the blow molding so as to achieve substantially uniform cooling of the entirety of the inner wall of the molding, the arrangement, location, number, and size of the introduction/discharge needles (pipes) are determined as adequate in consideration of the shape, etc. of the product molding. In the present invention, the pipes are advantageously provided separately in consideration of cooling efficiency. Therefore, they are advantageously provided through the mold wall so as to obtain more freedom with respect to location.

[0050] If necessary, means for advancing and retracting the cooling medium introduction needles (pipes) may be provided, an opening may be formed in the side the introduction needles (pipes), and rotation means may be provided for the opening.

[0051] Further, in the case in which a low-temperature cooling medium is fed, a device for cooling the medium may be installed and arranged to communicate with the cooling medium introduction needles (pipes) via a pipe.

[0052] The present invention will next be described in more detail by way of examples and comparative examples, which should not be construed as limiting the invention thereto.

Example 1

[0053] A blow molding was fabricated through blow molding performed under the following conditions.

1. Polypropylene resin composition serving as a raw material

1-1. Components of the composition

[0054]

1-1-1. Polypropylene = 65% by weight (product of Idemitsu Petrochemical Co., Ltd.; Idemitsu Polypro, E-100GM,

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MI: 0.6 g/10 min (230°C, 2.16 kgf)

1-1-2. High density polyethylene = 10% by weight (product of Idemitsu Petrochemical Co., Ltd.; Idemitsu Polyethylene, 750LB, MI: 0.03 g/10 min (190°C, 2.16 kgf), density: 0.95 g/cm³)

1-1-3. Ethylene-propylene copolymer elastomer = 15% by weight (product of Japan Synthetic Rubber Co., Ltd.;

EP07P, Mooney viscosity ML₁₊₄ (100°C): 77, ethylene content: 73% by weight)

1-1-4. Talc = 10% by weight (mean grain size: 1.5 µm, mean aspect ratio: 15)

1-2. Preparation of composition: The composition was prepared through melt-kneading.

1-3. Properties of composition: The properties of the composition were measured as follows:

[0055]

1-3-1. Crystallization temperature: 123°C

1-3-2. Melting point: 164°C

[0056] The crystallization temperature and the melting point were determined by use of a differential scanning calorimeter (DSC-7; manufactured by Perkin-Elmer) in accordance with JIS K7121. The resin composition was heated from room temperature at 10°C/min, and its melting point was measured. Subsequently, the composition was retained for 3 minutes at 230°C, and then cooled at 10°C/min, to thereby obtain its crystallization temperature.

2. Blow molding: Air spoiler for an automobile

[0057]

2-1. Shape: Blow cylindrical shape (1,400 mm x 200 mm x 30 mm)

2-2. Weight of the product: Approximately 2.0 kg

3. Molding conditions

[0058]

3-1. Molding machine: 90 mmØ blow molding machine (die: 100 mm in diameter, accumulator: 25 liters, clamping pressure: 60 tons, screw rotation: 40 rpm, motor load: 115A)

3-2. Molding temperature: cylinder: 230-190°C, crosshead: 190°C, die: 190°C, resin temperature: 220°C

4. Molds

[0059]

4-1. Heating means: The surface temperature was regulated to 128°C through circulation of a heating oil (150°C).

4-2. Mold inner surface: Polished surface of 0.2 S having a large number of degassing pores having a diameter of 50 µm (pitch: 10 mm).

5. Molding method

[0060] A parison of the above-mentioned crystalline resin was fed to the space between a set of molds and clamped; dry air at -35°C was blown into the parison through a cooling medium introduction needle formed through the wall of a mold so as to cause the parison to come into close contact with the mold inner surfaces; the introduction of the dry air was continued until the internal pressure of the parison reached 10 kg/cm²; 10 seconds later, the dry air was discharged from the parison through a cooling medium discharge needle formed through the wall of the mold so that the internal pressure of the parison became 3 kg/cm². The cooling medium introduction needle was provided in the mold so that it was positioned at a location 20 mm from one edge of the back side of an air spoiler (the side which serves as the back side when the air spoiler is attached to an automobile), whereas the cooling medium discharge needle was provided in the mold so that it was positioned at a location 20 mm from the other edge of the spoiler, so as to cause the cooling medium to flow in a single direction.

[0061] At the initial stage of the cooling of the parison, the temperature of the discharged air was 90°C. When the temperature of the discharged air dropped to 40°C, the introduction of the dry air was terminated; the remaining air

within the parison was discharged; the molds were opened; and a molding was removed from the molds.

6. Evaluation of blow molding

5 [0062]

6-1. Surface gloss of product: The surface gloss was measured under the conditions of incidence angle = 60° and light interception angle = 60° in accordance with JIS K7105. The surface gloss was found to be 95%.

10 6-2. "Hair" on the mold inner surface: Presence or absence of hair was visually checked, and no generation of hair was found.

6-3. Haze in the mold inner surface: The haze was evaluated according to the following criteria.

A: No haze

B: Difficult to visually determine

15 C: Visually observed (partially)

[0063] The rank was found to be A.

7. Evaluation of molding cycle

20

[0064] An average cycle time of molding was obtained from ten cycles of producing moldings; the cycle time is defined from the viewpoint of time at which a molding is removed from the molds to the point of time at which the molding is removed from the molds in the subsequent molding cycle. The average molding cycle time was found to be 210 seconds.

25 [0065] As shown by the above-mentioned evaluation results, blow moldings having excellent surface conditions were confirmed to be produced by the production method of the present invention. Further, the molding cycle time is comparable with those shown in Examples 3-7 below, which indicates that intentional and intensive cooling of the mold temperature is not always necessary.

30 Example 2

[0066] The procedure of Example 1 was repeated to produce a blow molding, except that the following conditions were used.

35 1. Blow molding: Wheel cap

[0067]

1-1-1. Shape = diameter: 400 mm, with seven through holes along the periphery, wall thickness: 3-4 mm

40 1-1-2. Weight of the product: Approximately 550 g

2. Molding conditions

[0068]

45

2-1. Molding machine: 90 mmØ blow molding machine (die: 160 mm in diameter, accumulator: 15 liters, clamping pressure: 60 tons, screw rotation: 40 rpm, motor load: 115A)

2-2. Molding temperature: cylinder: 230-190°C, crosshead: 210°C, die: 210°C, resin temperature: 220°C

50 3. Mold

[0069]

3-1. Mold inner surface temperature: The temperature was regulated to 120°C.

55

4. Molding method

[0070] A parison was fed to the space between a set of molds and clamped; dry air of room temperature was blown

into a portion within the parison corresponding to the central portion of a molding (wheel cap) via a pressurized fluid introduction needle formed through the wall of a mold so as to cause the parison come into close contact with the mold inner surfaces; the introduction of the dry air was terminated; dry air at -35°C was blown into three portions within the parison corresponding to the peripheral portions of the molding via cooling medium introduction needles formed through the wall of the mold until the internal pressure of the parison reached 7 kg/cm²; and the cooling medium was discharged from the parison through the same pressurized fluid introduction needle, through which the above-mentioned dry air of room temperature had been previously blown into the parison, while the internal pressure of the parison was maintained at 3.5 kg/cm² (with this procedure, the cooling medium was caused to flow from the peripheral portions to the central portion of the molding); 170 seconds later, the introduction of the -35°C dry air was terminated; the pressure within the parison was released; the molds were opened; and the molding was removed from the molds.

5. Evaluation of blow molding

[0071] The blow molding was evaluated in the same manner as in Example 1. The results include a surface gloss of 95%, no generation of "hair," and grade A evaluation with respect to haze.

Examples 3-7 and Comparative Examples 1-5

[0072] Blow moldings were fabricated in a manner similar to that described in Example 1, but by use of the following conditions.

1. Mold

[0073]

1-1. Heating means and cooling means: The surface temperature was regulated through circulation of a heating oil (150°C) and a cooling oil (60°C). The details the temperature regulation are shown in Table 1. The circulation of the heating oil and the cooling oil was performed via a common pipe, and, in this cooling method, fresh oil was fed after complete purging of the old oil.

1-2. Mold inner surfaces: Polished surface of 0.2 S having degassing pores whose diameter and pitch are as shown in Table 1.

2. Molding method

[0074] The molding method employed in Examples 3-7 was same as in Example 1 except that the steps of heating and cooling of molds were additionally performed as follows. Briefly, the molds were heated until clamping which followed mold opening and feeding of a parison. Subsequently, the molds were cooled until a molding was removed.

[0075] In Comparative Examples 1-5, molding was performed without provision of a cooling medium discharge needle.

3. Evaluation of molding and molding cycle

[0076]

3-1. Shape retainability at the time when the molded product is released: The shape retainability was visually evaluated according to the following criteria.

A: Deformation was not visually observed

B: Deformation that may adversely affect the product was not observed

C: A slight deformation was partially observed

D: Considerable distortion was observed

[0077] The results are shown in Table 1.

[0078] The surface gloss, presence and absence of "hair," haze, and molding cycle time were investigated in the same manner as in Example 1. The results are also shown in Table 1.

[0079] The results of evaluation showed that the products and methods of Examples 3-5 are excellent in every respect. Those of Examples 6 and 7 are excellent in terms of gloss and molding cycle time; however, they were second to Examples 3-5 with respect to haze in the surface. In contrast, none of Comparative Examples provided a satisfactory

level of gloss and excellent molding cycle time at the same time.

Table 1

	Mold temperature upon contact of parison (°C)	Mold temperature upon removal of molding (°C)	Dye: degassing pores		Forced cooling inside parison?	Shape retainability when molding is removed
			Diameter (μm)	Pitch (mm)		
Ex. 3	130	110	50	5	Yes	B
Ex. 4	130	100	50	5	Yes	B
Ex. 5	130	100	50	10	Yes	B
Ex. 6	130	100	50	50	Yes	B
Ex. 7	130	100	100	50	Yes	B
Comp. Ex. 1	60	60	50	5	No	A
Comp. Ex. 2	120	60	50	5	No	A
Comp. Ex. 3	130	60	50	5	No	A
comp. Ex. 4	130	80	50	5	No	A
Comp. Ex. 5	130	100	50	5	No	D
	Surface gloss of molding (%)	"Hair" on the surface of molding	Haze in the surface of molding	Molding cycle (sec)		
				Heating	Cooling	Total
Ex. 3	95	None	A	60	180	240
Ex. 4	95	None	A	120	180	300
Ex. 5	95	None	B	120	180	300
Ex. 6	95	None	C	120	180	300
Ex. 7	95	Slight	C	120	180	300
Comp. Ex. 1	20	None	A	0	120	150
Comp. Ex. 2	65	None	A	>240	>500	>780
Comp. Ex. 3	90	None	A	>240	>500	>780
comp. Ex. 4	95	None	A	>240	>500	>780
Comp. Ex. 5	—	—	—	—	—	—

Industrial applicability

[0080] Blow moldings produced through the production method or the apparatus of the present invention realize excellent mold transferability and, notwithstanding the method being a variation of blow molding, the blow moldings are provided with a high surface gloss of 90% or more. Also, despite a high level of glossiness of the blow moldings, the production method and apparatus excellently reduces the molding cycle time and provide satisfactory product quality and productivity. Further, production facilities as well as control of molding are simplified since heating and cooling cycles for the molds are substantially eliminated. In addition, since a high surface gloss is advantageously obtained, products requiring no secondary coating can be produced. Therefore, the production method and apparatus are applicable to manufacture of a broad range of products such as automobile parts, furniture, and bath/lavatory utensils.

Claims

1. A method of producing a blow molding comprising the steps of feeding a melt parison of crystalline resin into the space between molds, clamping the molds, blowing a pressurized fluid into the interior of the parison so as to cause the parison to come into close contact with the inner surfaces of the molds and to solidify the parison, wherein, while the parison and the mold inner surfaces are in close contact, the temperature of inner surfaces of the molds is maintained at a temperature within the range from a temperature 10°C lower than the crystallization temperature of the crystalline resin to the melting point of the crystalline resin, and the parison is removed from the molds after the parison is cooled through introduction thereinto or discharge therefrom, during or after blowing-in of the pressurized fluid, of a cooling medium whose temperature is not higher than room temperature.
2. The method according to Claim 1, wherein the molds have degassing pores having a diameter of 100 µm or less in the surfaces of the molds at intervals (a pitch) of 50 mm or less.
3. The method according to Claim 1 or 2, wherein the temperature of the mold inner surfaces falls within the crystallization temperature of the crystalline resin \pm 10°C when the parison and the mold inner surfaces are in close contact.
4. The method according to Claim 1 or 2, wherein introduction and discharge of the cooling medium are performed through an introduction port and a discharge port, respectively, which are provided at locations remote from each other.
5. The method according to Claim 1 or 2, wherein the cooling medium is air.
6. The method according to Claim 1 or 2, wherein the internal pressure of the parison as measured at the beginning of introduction of the cooling medium is at least 4 kg/cm², and subsequently, the internal pressure of the parison is reduced to a level lower than that as measured at the beginning of introduction of the cooling medium.
7. The method according to Claim 1 or 2, wherein the molds are cooled by use of a cooling means after the parison has been brought into close contact with the molds.
8. The method according to Claim 1 or 2, wherein the crystalline resin is a polypropylene resin.
9. Apparatus for the production of a blow molding which comprises:
 - a blow molding machine;
 - a forming mold which is used in combination with the blow molding machine for producing a blow molding, the forming mold having degassing pores having a diameter of 100 µm or less in the surface of the mold at intervals (a pitch) of 50 mm or less; and
 - means for introducing and discharging a cooling medium into or from a parison formed through the mold.
10. The apparatus according to Claim 9, wherein the means for introducing and discharging the cooling medium are introduction pipe and discharge pipe, respectively, which penetrate the mold and which are provided at locations remote from each other.

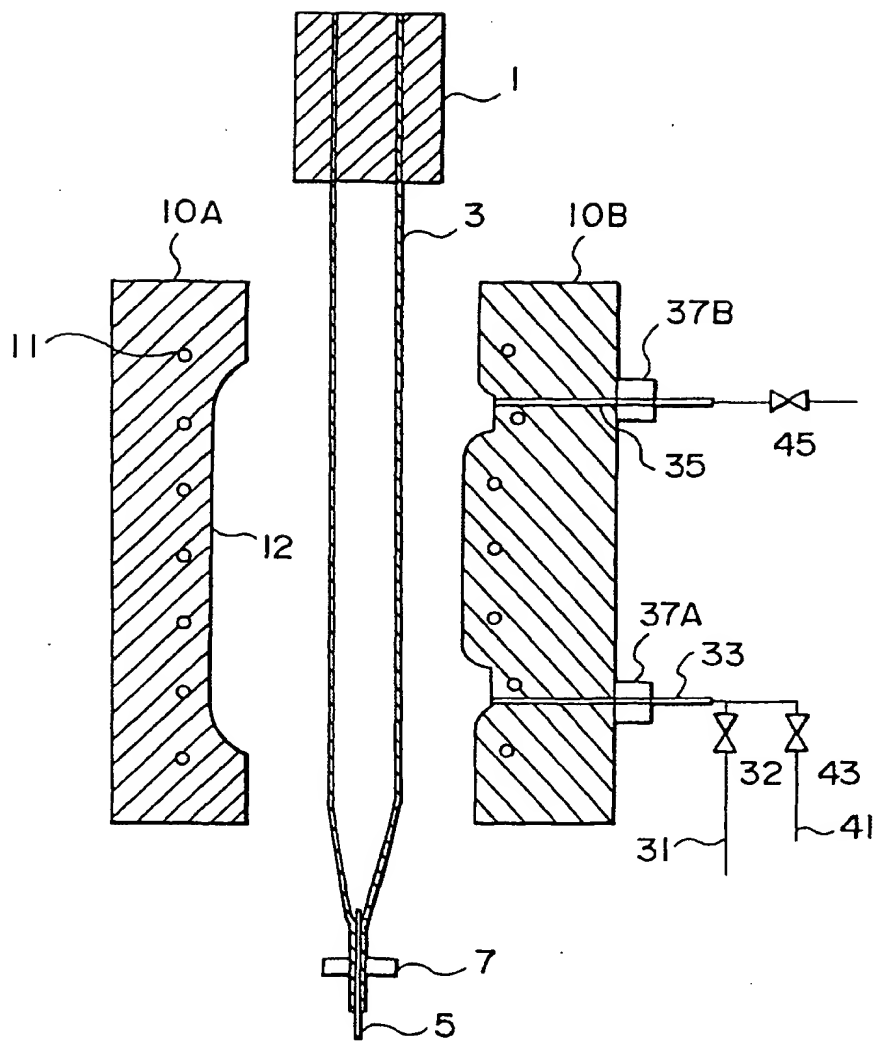


FIG. 1

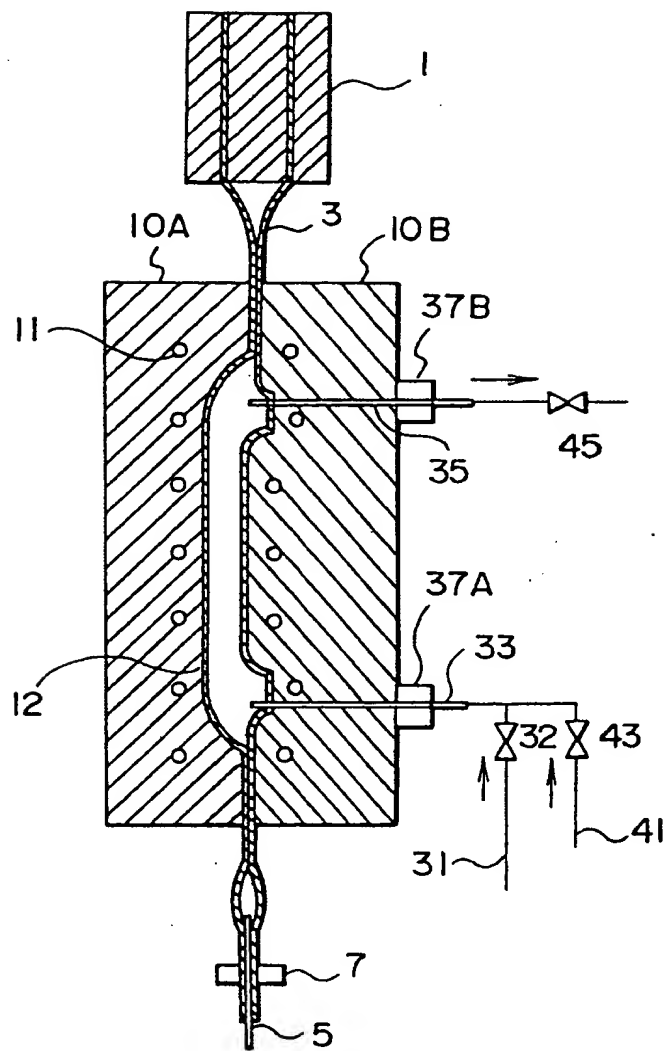


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/01751

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ B29C49/64, B29C49/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ B29C49/00-49/80

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1997
 Kokai Jitsuyo Shinan Koho 1971 - 1997
 Toroku Jitsuyo Shinan Koho 1994 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 60-112419, A (Mitsubishi Plastics Industries Ltd.), June 18, 1985 (18. 06. 85), Claim; Figs. 1 to 3 (Family: none)	1, 3, 4, 5
Y		7
A		2, 6, 8-10
Y	JP, 6-23754, A (Centro Sviluppo Settori Impiego Societa a Responsabilita Limitata), February 1, 1994 (01. 02. 94), Claim; Figs. 1, 2 & IT, 1244146, A & EP, 483849, B1	7
A	JP, 4-336224, A (Showa Denko K.K.), November 24, 1992 (24. 11. 92) (Family: none)	1 - 10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

June 25, 1997 (25. 06. 97)

Date of mailing of the international search report

July 8, 1997 (08. 07. 97)

Name and mailing address of the ISA/

Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

be, the additives may be mixed with the polymers in extruders while the polymers are pelletized.

[0125] The mixing ratio of the inert gas to the swelling solvent may be such that the swelling solvent is in the mixed solvent gas in an amount of not smaller than 1 % by volume, preferably not smaller than 5 % by volume.

(iii) Additives in Polymerization:

[0126] In the solid-phase polymerization or the swollen solid-phase polymerization in the invention, optionally but preferably used is a terminal-stopping agent such as p-t-butylphenol, p-cumylphenol, p-phenylphenol or the like. If further desired, any known chain-branching agent may be used. If still desired, any known antioxidant may be added to the reaction system. As the antioxidant, preferred are phosphorus-containing antioxidants.

(iv) Oxygen Concentration and Water Concentration in Vapor Phase in Polymerization System:

[0127] In the second and third aspects of the invention, the oxygen concentration in the vapor phase in the polymerization reaction system is preferably not larger than 2 ppm. To the fourth aspect of the invention, however, this condition is indispensable. The oxygen concentration is more preferably not larger than 1 ppm, even more preferably not larger than 0.5 ppm. It is desirable that the water concentration in the reaction system is not larger than 2 ppm, more preferably not larger than 1 ppm. If the oxygen concentration in the polymerization reaction system is larger than 2 ppm, the polymers to be obtained will be often colored and, in addition, their thermal stability is poor. On the other hand, if the water concentration therein is larger than 2 ppm, such is undesirable since the polymers being produced will be hydrolyzed and since the activity of the catalyst being used will be lowered.

[0128] The method for lowering the oxygen concentration in the reaction system to be not more than 2 ppm and for lowering the water concentration therein also to be not more than 2 ppm is not specifically defined. For example, an oxygen-removing duct equipped with an oxygen filter or the like and a water-removing duct equipped with a moisture filter or the like may be disposed before the polymerization reactor in the production line.

[0129] The polycarbonates as obtained according to the present invention may be mixed with any known additives of, for example, plasticizer, pigment, lubricating agent, mold-releasing agent, stabilizer, inorganic filler, etc., before they are used. Further if desired, any known antioxidant may be added to the reaction system of producing the polycarbonates. As the antioxidant, preferably used are phosphorus-containing antioxidants.

[0130] The polycarbonates may be blended with any other polymers, such as polyolefins, polystyrenes, polyesters, polysulfonates, polyamides, polyphenylene ethers, etc. In particular, they are effectively blended with polyphenylene ethers, polyether nitriles, terminal-modified polysiloxane compounds, modified polypropylenes, modified polystyrenes and the like having OH, COOH, NH₂ or the like group at their terminals.

[0131] The invention will be described in more detail hereinafter, which, however, are not whatsoever intended to restrict the scope of the invention.

Examples 1 to 4, and Comparative Examples 1 and 2:

[0132] 22.8 g (0.1 mols) of bisphenol A (BPA) and 23.5 g (0.11 mols) of diphenyl carbonate were put into a 100-ml nickel steel autoclave equipped with a stirrer, along with a catalyst of which the type and the amount are shown in Table 1 below, and purged with argon five times in all. Next, the mixture was heated at 180°C and reacted for 30 minutes in the argon atmosphere. Next, this was further heated up to 210°C and reacted for 30 minutes with being gradually vacuumed up to 100 mmHg; then this was still further heated up to 240°C and reacted for 30 minutes with being gradually vacuumed up to 10 mmHg; then this was still further heated up to 270°C and reacted for 30 minutes with being vacuumed up to 2 mmHg; and finally, this was still further heated up to 290°C and reacted for 30 minutes with being vacuumed up to 0.3 mmHg. In that manner, the reaction was finished.

[0133] Next, the viscosity-average molecular weight of the viscous transparent condensate (polycarbonate) thus produced in the autoclave was measured. The condensate was press-molded into test discs having a thickness of 1 mm and a diameter of 10 mm, which were then exposed to steam at 121°C for 48 hours. The decrease in the viscosity-average molecular weight of the exposed sample was obtained, from which the steam resistance of the sample was evaluated.

[0134] The viscosity-average molecular weight M_v is obtained according to the following equation, in which $[\eta]$ indicates the limiting viscosity in methylene chloride at 20°C.

$$[\eta] = 1.23 \times 10^{-5} \times M_v^{0.83}$$

[0135] The condensate was subjected to a high-temperature high-humidity test. Briefly, the condensate was dried at 120°C for 5 hours or longer, and press-molded into test discs having a diameter of 12 cm and a thickness of 1.2 mm.

which were exposed to heat at 80°C and 85 % RH for 48 hours. The thus-exposed discs were observed with a transmission polarizing microscope, and the number of white spots having a diameter of not smaller than 10 µm seen in each sample was counted.

[0136] The data obtained are shown in Table 2.

Example 5:

[0137] 22.8 g (0.1 mols) of bisphenol A (BPA) and 23.5 g (0.11 mols) of diphenyl carbonate were put into a 100-ml nickel steel autoclave equipped with a stirrer, along with a catalyst of which the type and the amount are shown in Table 1 below, and purged with argon five times in all. Next, the mixture was heated at 180°C and reacted for 30 minutes in the argon atmosphere. Next, this was further heated up to 210°C and reacted for 30 minutes with being gradually vacuumed up to 100 mmHg; then this was still further heated up to 240°C and reacted for 30 minutes with being gradually vacuumed up to 10 mmHg, and then reacted for 30 minutes with being vacuumed up to 2 mmHg; then this was still further heated up to 260°C and reacted for 30 minutes; and finally, this was still further heated up to 270°C and reacted for 30 minutes with being vacuumed up to 0.3 mmHg. In that manner, the reaction was finished. The polycarbonate thus produced herein was tested in the same manner as in Example 1. The data obtained are shown in Table 2.

Table 1

	Catalyst (a)		Catalyst (b)	
	Type	Amount (mol/mol of BPA)	Type	Amount (mol/mol of BPA)
Example 1	TBTB	2.5×10^{-4}	TPTB	1×10^{-5}
Example 2	TBTB	2.5×10^{-4}	BPTB	1×10^{-5}
Example 3	TBTB	2.5×10^{-4}	MOPTB	1×10^{-5}
Example 4	TBTB	2.5×10^{-4}	TPPP	1×10^{-5}
Example 5	TBTB	2.5×10^{-4}	HPTB	1×10^{-5}
Comparative Example 1	TBTB	2.5×10^{-4}	-	-
Comparative Example 2	TMAH	2.5×10^{-4}	NaOH	1×10^{-6}
(Notes) TBTB: Tetrabutylphosphonium tetraphenyl borate (Na < 10 ppm, Ca < 10 ppm, K < 10 ppm, Mg < 10 ppm) TMAH: Tetramethylammonium hydroxide (Na < 1 ppb, Ca < 1 ppb, K < 1 ppb) TPTB: Tetraphenylphosphonium tetraphenyl borate (Na < 1 ppm, Ca < 1 ppm, K < 1 ppm) BPTB: Biphenyltriphenylphosphonium tetraphenyl borate (Na < 1 ppm, Ca < 1 ppm, K < 1 ppm) MOPTB: Methoxyphenyltriphenylphosphonium tetraphenyl borate (Na < 1 ppm, Ca < 1 ppm, K < 1 ppm) TPPP: Tetraphenylphosphonium phenoxide (Na < 1 ppm, Ca < 1 ppm, K < 1 ppm) HPTB: Cyclohexyltriphenylphosphonium tetraphenyl borate (Na < 10 ppm, Ca < 10 ppm, K < 10 ppm, Mg < 10 ppm)				

Table 2

	Viscosity-Average Molecular Weight (Mv)	Steam Resistance Test (Δ Mv)	High-Temperature High- Humidity Test (white spots/sample)
Example 1	16,000	600	1
Example 2	17,500	700	2
Example 3	19,000	700	2
Example 4	18,000	800	1
Example 5	15,000	500	0
Comparative Example 1	5,100	-	-
Comparative Example 2	20,000	3000	100 or more

Examples 6 to 8, and Comparative Examples 3 and 4:

[0138] 228 g (1.0 mol) of bisphenol A (BPA) and 225 g (1.05 mols) of diphenyl carbonate were put into a one-liter nickel steel autoclave equipped with a stirrer, along with a catalyst which is shown in Table 3 below, and purged with argon five times in all. Next, the mixture was heated at 180°C and reacted for 30 minutes in the argon atmosphere. Next, this was further heated up to 240°C and reacted over a period of 120 minutes with being vacuumed up to 8 mmHg; then this was still further heated up to 270°C and reacted over a period of 30 minutes with being vacuumed up to 7 mmHg; and finally, this was further vacuumed up to 1 mmHg and reacted for 5 minutes. After the reaction, the reactor was purged with argon to be at the atmospheric pressure, and the prepolymer produced therein was taken out and ground.

[0139] The number-average molecular weight of the prepolymer (as calculated from $^1\text{H-NMR}$) was 3500, and the hydroxyl terminal fraction thereof was 49.5 %.

[0140] The thus-obtained prepolymer was dissolved in methylene chloride, to which was added paraxylene whereby was formed a powdery precipitate in the solution. This was concentrated into a solid, and then dried in vacuum to obtain a powdery prepolymer. One g of this powder was put into a SUS tube having a diameter of 10 mm and a length of 200 mm, into which was introduced nitrogen at 220°C and at a flow rate of 50 ml/min. In that condition, the prepolymer was subjected to solid-phase polymerization for 90 minutes. The polycarbonate thus obtained as a result of the solid-phase polymerization was tested in the same manner as in Example 1. The data obtained are shown in Table 4.

Examples 9 and 10:

[0141] Polycarbonates were produced in the same manner as in Examples 7 and 8, except that paraxylene but not nitrogen was introduced into the tube at a flow rate of 20 ml/min. The polycarbonates thus produced in the swollen solid-phase polymerization were tested in the same manner as in Example 1. The data obtained are shown in Table 4.

Table 3

	Catalyst (a)		Catalyst (b)	
	Type	Amount (mol/mol of BPA)	Type	Amount (mol/mol of BPA)
Example 6	TBTB	2.5×10^{-4}	TPTB	1×10^{-5}
Example 7	TBTB	2.5×10^{-4}	BPTB	1×10^{-5}
Example 8	TBTB	2.5×10^{-4}	MOPTB	1×10^{-5}
Example 9	TBTB	2.5×10^{-4}	TPPP	1×10^{-5}
Example 10	TBTB	2.5×10^{-4}	HPTB	1×10^{-5}
Comparative Example 3	TBTB	2.5×10^{-4}	-	-

Example 20:

[0146] 9.2 mols of bisphenol A, 9.4 liters of an aqueous solution of 2.0 N sodium hydroxide, and 8 liters of methylene chloride were put into a 50-liter container equipped with a stirrer, and stirred, into which a large excess amount of phosgene was introduced for 30 minutes.

[0147] Next, 0.79 mols of phenol was reacted with this, and 0.4 mols of bisphenol A, 0.022 mols of triethylamine and 4.5 liters of an aqueous solution of 0.2 N sodium hydroxide were added thereto and reacted for 40 minutes. The aqueous phase and the organic phase thus formed were separated from each other. Thus was obtained a methylene chloride solution of a polycarbonate oligomer.

[0148] 8 liters of the methylene chloride solution of the polycarbonate oligomer was mixed with 3.9 mols of bisphenol A, 400 g of an aqueous solution of 7.25 wt.% sodium hydroxide, 0.017 mols of triethylamine and 8 liters of methylene chloride, and reacted for 60 minutes with stirring them at 500 rpm.

[0149] After the reaction, the aqueous phase and the organic phase thus formed were separated from each other, and the organic phase was washed with pure water, an alkali (aqueous solution of 0.01 N sodium hydroxide), an acid (0.1 N hydrochloric acid) and pure water in that order. Thus was obtained an organic solvent solution of a polycarbonate prepolymer. A part of this was sampled, from which was removed methylene chloride to obtain a powdery prepolymer. According to the test method mentioned above, the viscosity-average molecular weight of the powdery prepolymer was measured, and it was 8,700.

[0150] The prepolymer thus formed in the organic solvent solution was ground, while the solvent methylene chloride was evaporated away, to obtain a powdery prepolymer.

[0151] This was polymerized in the same manner as in Example 11 to produce a polycarbonate. The resulting product, polycarbonate was tested in the same manner as in Example 11. The data obtained are shown in Table 5.

Comparative Example 9:

[0152] In the same manner as in Comparative Example 5, except that the prepolymer obtained in Example 20 was used, a polycarbonate was produced and tested. The data obtained are shown in Table 5. Example 21:

[0153] In the same manner as in Example 14, except that the prepolymer obtained in Example 20 was used, a polycarbonate was produced and tested. The data obtained are shown in Table 5.

[0154] In the stay burning test in Table 5, each polycarbonate sample was exposed to a nitrogen stream atmosphere at 340°C for 90 minutes, and a 2.4 % methylene chloride solution of the thus-exposed sample was put into a quartz cell having a photo-guide length of 57 mm, through which the color of the sample was measured with a color meter, SM-3 Model (manufactured by Suga Testers Co.). From the data measured, obtained was the YI (yellow index) of the sample.

Table 5

	Polymerization Catalyst		Viscosity-Average Molecular Weight (Mv)	High-Temperature High-Humidity Test (white spots/sample)	Stay Burning Test (YI)
	Type	Amount (mol/mol of BPA)			
Example 11	TPP	1×10^{-3}	14,300	2	4
Example 12	TBP	5×10^{-3}	15,000	5	6
Example 13	TPO	1×10^{-3}	14,600	3	7
Example 14	TMAH	1×10^{-3}	16,700	5	7
Example 15	TBTB	1×10^{-4}	14,800	4	5
Example 16	DBN	1×10^{-3}	16,100	4	-
Comparative Example 5	NaOH	1×10^{-6}	9,900	-	15
Comparative Example 6	-	-	8,700	-	6
Example 17	TPO	1×10^{-3}	14,300	3	-
Example 18	TMAH	1×10^{-3}	16,100	4	8

Table 5 (continued)

	Polymerization Catalyst		Viscosity-Average Molecular Weight (Mv)	High-Temperature High-Humidity Test (white spots/sample)	Stay Burning Test (YI)
	Type	Amount (mol/mol of BPA)			
Example 19	TBTB	1×10^{-6}	14,600	4	9
Comparative Example 7	NaOH	1×10^{-2}	19,600	100 or more	16
Comparative Example 8	-	1×10^{-3}	6,700	-	6
Example 20	TPO	1×10^{-3}	14,800	2	7
Example 21	TMAH	1×10^{-3}	16,700	4	8
Comparative Example 9	NaOH	1×10^{-6}	9,600	-	17
(Notes) TPP: Triphenyl phosphate, TBP: Tributylphosphine, TPO: Triphenylphosphine oxide, DBN: 1,5-Diazabicyclo[4,3,0]-5-nonene, TMAH, TBTB: Same as in Table 1.					

Examples 22 and 23:

[0155] 228 g (1.0 mol) of bisphenol A (BPA), 225 g (1.05 mols) of diphenyl carbonate and 0.5 mmols of tetramethyl-ammonium hydroxide were put into a one-liter nickel steel autoclave equipped with a stirrer, and purged with argon five times in all. Next, the mixture was heated at 180°C and reacted for 30 minutes in the argon atmosphere. Next, this was further heated up to 240°C and reacted over a period of 120 minutes with being vacuumed up to 8 mmHg; then this was still further heated up to 270°C and reacted over a period of 30 minutes with being vacuumed up to 7 mmHg; and finally, this was further vacuumed up to 1 mmHg and reacted for 5 minutes. After the reaction, the reactor was purged with argon to be at the atmospheric pressure, and the prepolymer produced therein was taken out and ground.

[0156] The number-average molecular weight of the prepolymer (as calculated from $^1\text{H-NMR}$) was 4500. The hydroxyl terminal fraction of the prepolymer was 49.5 %.

[0157] The thus-obtained prepolymer was dissolved in methylene chloride, to which were added the catalyst shown in Table 6 below and then paraxylene whereby was formed a powdery precipitate in the solution. This was concentrated into a solid, and then dried in vacuum to obtain a powdery prepolymer. One g of this powder was put into a SUS tube having a diameter of 10 mm and a length of 200 mm, into which was introduced nitrogen at 220°C and at a flow rate of 50 ml/min. In that condition, the prepolymer was subjected to solid-phase polymerization for 90 minutes. In this step, an oxygen-removing duct (Indicating Oxygen Trap, manufactured by GL Science Co.) and a water-removing duct (Moisture Filter, manufactured by GL Science Co.) were disposed before the polymerization reactor in the production line, and the oxygen concentration in the reaction system was controlled to be not larger than 1.0 ppm and the water concentration therein was to be not larger than 0.5 ppm. The polycarbonate obtained as a result of the reaction was exposed to a nitrogen stream atmosphere at 340°C for 90 minutes, and its yellow index (YI) was measured (stay burning test). In the same manner as in Example 6, the viscosity-average molecular weight of the polycarbonate was measured. The data obtained are shown in Table 6.

Example 24:

[0158] The same process as in Example 22 was repeated, except that only the oxygen-removing duct (Indicating Oxygen Trap, manufactured by GL Science Co.) was disposed but the water-removing duct was not. The data of the polycarbonate obtained are shown in Table 6. Comparative Example 10:

[0159] The same process as in Example 22 was repeated, except that the oxygen-removing duct and the water-removing duct were not used. In this, the oxygen concentration in the reaction system was 5 ppm, and the water concentration therein was 5 ppm. The data of the polycarbonate obtained are shown in Table 6.

Examples 25 and 26:

[0160] The same process as in Examples 22 and 23 was repeated, except that paraxylene was introduced into the SUS tube at a flow rate of 20 g/hr in place of nitrogen introduced thereinto at a flow rate of 50 ml/min. Prior to being introduced into the SUS tube, paraxylene was distilled under normal pressure in nitrogen that had been passed through an oxygen-removing duct (Indicating Oxygen Trap, manufactured by GL Science Co.) and a water-removing duct (Moisture Filter, manufactured by GL Science Co.), and bubbled with the same nitrogen for 12 hours. In this, the oxygen concentration in the reaction system was not larger than 1.0 ppm, and the water concentration therein was 1 ppm. The data of the polycarbonates obtained are shown in Table 6.

Comparative Example 11:

[0161] The same process as in Example 25 was repeated, except that commercially-available paraxylene (manufactured by Wako Pure Chemicals Co.) was used. In this, the oxygen concentration in the reaction system was larger than 5 ppm, and the water concentration therein was larger than 10 ppm. The data of the polycarbonate obtained are shown in Table 6.

Example 27:

[0162] 9.2 mols of bisphenol A, 9.4 liters of an aqueous solution of 2.0 N sodium hydroxide, and 8 liters of methylene chloride were put into a 50-liter container equipped with a stirrer, and stirred, into which a large excess amount of phosgene was introduced for 30 minutes.

[0163] Next, 0.79 mols of phenol was reacted with this, and 0.4 mols of bisphenol A, 0.022 mols of triethylamine and 4.5 liters of an aqueous solution of 0.2 N sodium hydroxide were added thereto and reacted for 40 minutes. The aqueous phase and the organic phase thus formed were separated from each other. Thus was obtained a methylene chloride solution of a polycarbonate oligomer.

[0164] 8 liters of the methylene chloride solution of the polycarbonate oligomer was mixed with 3.9 mols of bisphenol A, 400 g of an aqueous solution of 7.25 wt.% sodium hydroxide, 0.017 mols of triethylamine and 8 liters of methylene chloride, and reacted for 60 minutes with stirring them at 500 rpm.

[0165] After the reaction, the aqueous phase and the organic phase thus formed were separated from each other, and the organic phase was washed with pure water, an alkali (aqueous solution of 0.01 N sodium hydroxide), an acid (0.1 N hydrochloric acid) and pure water in that order. Thus was obtained an organic solvent solution of a polycarbonate prepolymer. A part of this was sampled, from which was removed methylene chloride to obtain a powdery prepolymer. According to the test method mentioned above, the viscosity-average molecular weight of the powdery prepolymer was measured, and it was 8,700.

[0166] The prepolymer thus formed in the organic solvent solution was ground, while the solvent methylene chloride was evaporated away, to obtain a powdery prepolymer.

[0167] This was polymerized in the same manner as in Example 22 to produce a polycarbonate. The data of the resulting product, polycarbonate are shown in Table 6.

Comparative Example 12:

[0168] The same process as in Example 27 was repeated, except that the oxygen-removing duct and the water-removing duct were not used. In this, the oxygen concentration in the reaction system was 5 ppm, and the water concentration therein was 5 ppm. The data of the polycarbonate obtained are shown in Table 6.

Table 6

	Polymerization Catalyst		Viscosity-Average Molecular Weight (Mv)	Stay Burning Test (YI)
	Type	Amount (mol/mol of BPA)		
Example 22	HPTB	1×10^{-5}	23,300	10
Example 23	BPTB	1×10^{-5}	23,800	12

Table 6 (continued)

	Polymerization Catalyst		Viscosity-Average Molecular Weight (Mv)	Stay Burning Test (YI)
	Type	Amount (mol/mol of BPA)		
Example 24	HPTB	1×10^{-5}	20,900	10
Example 25	HPTB	1×10^{-5}	18,000	9
Example 26	BPTB	1×10^{-5}	18,000	9
Example 27	HPTB	1×10^{-5}	19,100	7
Comparative Example 10	HPTB	1×10^{-5}	24,700	24
Comparative Example 11	HPTB	1×10^{-3}	17,400	37
Comparative Example 12	HPTB	1×10^{-5}	18,400	25
(Notes)				
HPTB: Cyclohexyltriphenylphosphonium tetraphenyl borate				
BPTB: Biphenyltriphenylphosphonium tetraphenyl borate				

INDUSTRIAL APPLICABILITY

[0169] According to the method of the invention, high-quality polycarbonates having good appearance, high heat resistance and high hydrolysis resistance can be obtained extremely efficiently.

[0170] As having good properties such as those noted above, the polycarbonates obtained according to the method of the invention are favorably used in various fields, for example, in the field of electric and electronic appliances, in the field of automobiles, in the field of optical materials (for example, as materials for optical discs and photomagnetic discs), and in other various industrial fields.

Claims

1. A method for producing polycarbonates through melt transesterification, wherein is used a catalyst comprising (a) a phosphorus-containing basic compound and (b) a quaternary phosphonium salt having one or more groups selected from aryl groups and branched alkyl groups, provided that, when the phosphorus-containing basic compound (a) is a quaternary phosphonium salt, it differs from the quaternary phosphonium salt (b).
2. The method for producing polycarbonates as claimed in claim 1, wherein the phosphorus-containing basic compound (a) is a quaternary phosphonium salt in which the carbon atom directly bonding to the phosphorus atom does not have a branched structure.
3. Polycarbonates for optical materials, which are produced in the method of claim 1 or 2.
4. A method for producing polycarbonates through transesterification, which comprises pre-polymerization to prepare polycarbonate prepolymers followed by final polymerization of said prepolymers in a solid phase or in a swollen solid phase to produce the products, polycarbonates, and which is characterized in that a catalyst comprising (a) a phosphorus-containing basic compound and (b) a quaternary phosphonium salt having one or more groups selected from aryl groups and branched alkyl groups, provided that, when the phosphorus-containing basic compound (a) is a quaternary phosphonium salt, it differs from the quaternary phosphonium salt (b), is used in the pre-polymerization and in the final polymerization.
5. A method for producing polycarbonates through transesterification, which comprises pre-polymerization to prepare polycarbonate prepolymers followed by final polymerization of said prepolymers in a solid phase or in a swollen solid phase to produce the products, polycarbonates, and which is characterized in that a catalyst comprising (a) a phosphorus-containing basic compound is used in the pre-polymerization and a catalyst comprising (b) a quaternary phosphonium salt having one or more groups selected from aryl groups and branched alkyl groups, provided that, when the phosphorus-containing basic compound (a) is a quaternary phosphonium salt, it differs from the

quaternary phosphonium salt (b), is used in the final polymerization.

6. The method for producing polycarbonates as claimed in claim 4 or 5, wherein the phosphorus-containing basic compound (a) is a quaternary phosphonium salt in which the carbon atom directly bonding to the phosphorus atom does not have a branched structure.
7. Polycarbonates for optical materials, which are produced in the method of any one of claims 4 to 6.
8. A method for producing polycarbonates, which comprises preparing polycarbonate prepolymers in pre-polymerization followed by polymerizing said prepolymers in a solid phase or in a swollen solid phase in the presence of a catalyst of a tri-valent or penta-valent phosphorus compound.
9. A method for producing polycarbonates, which comprises preparing polycarbonate prepolymers in pre-polymerization followed by polymerizing said prepolymers in a solid phase or in a swollen solid phase in the presence of a catalyst of a nitrogen-containing organic basic compound.
10. Polycarbonates for optical materials, which are produced in the method of claim 8 or 9.
11. A method for producing polycarbonates by polymerizing polycarbonate prepolymers in a solid phase or in a swollen solid phase, wherein said prepolymers are polymerized in a vapor-phase atmosphere having an oxygen concentration of not larger than 2 ppm.
12. A method for producing polycarbonates by polymerizing polycarbonate prepolymers in a solid phase or in a swollen solid phase, wherein said prepolymers are polymerized in a vapor-phase atmosphere having an oxygen concentration of not larger than 2 ppm and a water concentration of not larger than 2 ppm.
13. The method for producing polycarbonates as claimed in claim 11 or 12, wherein a catalyst of a nitrogen-containing organic basic compound is used in preparing the polycarbonate prepolymers.
14. The method for producing polycarbonates as claimed in any one of claims 11 to 13, wherein polycarbonate prepolymers are prepared and then polymerized in a solid phase or in a swollen solid phase in the presence of a catalyst of a quaternary phosphonium salt.
15. The method for producing polycarbonates as claimed in any one of claims 11 to 14, which comprises transesterification of a dihydroxy compound and a dicarbonate to produce the polycarbonates.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/02107

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁶ C08G64/00, C08G64/18, C08G64/30		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl ⁶ C08G64/00-C08G64/42		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1997		
Kokai Jitsuyo Shinan Koho 1971 - 1997		
Toroku Jitsuyo Shinan Koho 1994 - 1997		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 7-62074, A (Mitsubishi Chemical Corp.), March 7, 1995 (07. 03. 95), Claim; Par. Nos. (0022), (0023), (0028), (0033)	1 - 10
Y	Claim; Par. Nos. (0022), (0023), (0028), (0033) (Family: none)	11 - 15
Y	JP, 7-26010, A (Idemitsu Petrochemical Co., Ltd.), January 27, 1995 (27. 01. 95), Claim; Par. Nos. (0004), (0047), (0048) & WO, 9502006, A & EP, 708128, A1 & US, 5650480, A	11 - 15
X	JP, 7-247354, A (Mitsubishi Gas Chemical Co., Inc.), September 26, 1995 (26. 09. 95), Claim; Par. Nos. (0025), (0026), (0032) (Family: none)	1, 2
	JP, 7-109346, A (Mitsubishi Gas Chemical Co., Inc.),	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "T" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search September 11, 1997 (11. 09. 97)		Date of mailing of the international search report September 24, 1997 (24. 09. 97)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)